Quantitative Observations of the Behavior of Anomalous Low
Altitude ClO in the Antarctic Spring Stratosphere, 1987

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During the second National Ozone Expedition we carried out ground-based
observations at McMurdo Station Antarctica which resulted in a second season's
measurement of abnormally large amounts of chlorine monoxide in the antarctic
spring stratosphere. Our original measurements of 1986, in which the presence of
this anomalous layer was first discovered (R.L.de Zafra, et al. 1987 and
P.Solomon, et al., 1987), were limited in low altitude recovery of the ClO
mixing ratio profile by the restrictions of the spectral bandwidth (256 MHz)
which was used to measure the pressure-broadened ClO emission line shape. Our
1987 measurements were marked by the use of twice the spectral bandpass employed
the previous year, and allow a better characterization of the ClO mixing ratio
profile in the critical altitude range 18-25 km. In-situ aircraft measurements
of ClO made over the Palmer Peninsula during August and September of 1987 by
Anderson, et al. effectively determined the important question of the ClO mixing
ratio profile at altitudes inaccessible to our technique, below ~18 to 18.5
km. These flights did not penetrate further than 72°S, however, (vs 78°S for
McMurdo) and were thus limited to coverage near the outer boundaries of the
region of severest ozone depletion over Antarctica in 1987, did not reach an
altitude convincingly above that of the peak mixing ratio for ClO, and were not
able to make significant observations of the diurnal variation of ClO. The two
techniques, and the body of data recovered by each, thus complement one another
in producing a full picture of the anomalous ClO layer intimately connected with
the region of antarctic springtime ozone depletion. In this talk we shall
present an analysis of the mixing ratio profile from ~18 to 45 km, the diurnal
behavior, and briefly comment on the secular change in ClO over McMurdo Station
during September and early October 1987.

The 1987 Antarctic spring vortex was markedly more regular in shape and
more closely centered on the pole than in 1986, or in fact during other recent
years. Stratospheric temperatures were also significantly and consistently lower
at the stratopause than in 1986 (Hofmann, et al, private communication) and
ozone depletion was more severe than ever before recorded. Conditions at ground
level at McMurdo were rather less stable than in 1986, however, and observations
were hampered by more frequent storms and by generally higher tropospheric
opacity due to higher ground temperatures and greater water vapor content. Our
observations for 1987 are consequently of shorter overall duration - from
September 8 to October 13 - and more frequently interrupted or rendered of poorer
quality by marginal observing conditions than in 1986. We shall concentrate our
attention here on data taken over the period Sept. 20-24 for a detailed
discussion of the mixing ratio profile,the peak mixing ratio for ClO, and the
diurnal behavior. Some conclusions will be drawn with respect to the secular
trend during the period from Sept.8 to Oct.13, using data in blocks averaged
over several days each.

We employ high-resolution spectral measurements of the pressure broadened
line shape and intensity of the 278 GHz (1.1 mm) rotational emission line of
ClO, using a cryogenically cooled mm-wave heterodyne receiver coupled to a
filterbank spectrometer having 512 contiguous channels of 1 MHz bandwidth each.

The pressure-broadening coefficient for the 278 GHz line of ClO is about 3 MHz/mb (hwhm for a Lorentzian lineshape) so that well-resolved line shapes can be measured over an altitude range of ~17 to 45 km (or ~80 to 1 mb, with respect to the antarctic pressure profile). The sum of emission line intensities over all contributing stratospheric layers yields a pressure-broadened non-Lorentzian line shape which can be deconvolved against measured pressure and temperature profiles to recover a mixing ratio profile for ClO or any other detected species. The accuracy with which this can be achieved depends critically on the signal/noise ratio of the data, and also varies with altitude and with the actual mixing ratio profile. Discussion of the accuracy with which mixing ratio profiles may be retrieved from our 1987 data, for the prevailing conditions, is covered in a companion paper at this workshop (P. Solomon, et al.).

Deconvolutions are carried out by a modified Chahine-Twomey algorithm, in which an initial mixing ratio profile is iteratively modified to yield successively better fits between the resulting synthesized line shape and the experimental data. This proceedure decreases rapidly in sensitivity at low (<~18 km) and high (>~45 km) altitudes: for this reason, we have chosen to assume an upper limit of 0.3 ppbv for the ClO mixing ratio at 15 km, in approximate agreement with in situ ER-2 aircraft measurements, to assist in achieving a reasonable lower altitude profile for the work presented in this paper. The assumption of one-third this value at 15 km has a negligible effect in altering the resultant retrieved profiles. Above 15 km, the profiles are determined by the deconvolution process. The effect of choosing different initial profile shapes between 15 and 25 km on the final retrieved profile has also been explored and is discussed elsewhere (P.Solomon, et al., this workshop): to summarize, maximum mixing ratio and the altitude at which it occurs are altered by no more than 20% and 10% respectively by the use of initial mixing ratio profiles differing by as much as a factor of 5.

Our result for the mid-day mixing ratio profile for the period Sept.20-24 is shown in Fig.1b, retrieved from the emission lineshape shown in Fig.1a. The mixing ratio profile is strongly separated into two distinct layers, a 'normal' high altitude component peaking around 37 km, and an anomalous low altitude layer never seen at tropical or mid latitudes, and exhibiting a mixing ratio in excess of 100 times that normally found (Brune, et al., 1988) at mid latitudes in this altitude range . This anomalous low altitude component is responsible for the broad wings in the lineshape of Fig.1a.

We find the peak mixing ratio to be 1.8 (+.5,-.9) parts per billion by volume and to occur at an altitude of 19 $\pm$ 1 km. The vertical column of ClO from 15 to 27 km derived from the profile of Fig.1b is 2.1 $\pm$ 0.5 x $10^{15}$/cm$^2$. The error margins quoted here are intended to include both uncertainties in intensity calibration (~12 %) and deconvolution accuracy.

The low altitude component shows a strong diurnal dependence, as exhibited in Fig.2, where data for Sept.20-24 has been averaged and binned in 2-hour time blocks starting 2 hours before dawn (defined at 20 km) and ending 6 hours after sunset. (The smooth curves fitted to the data are synthesized from mixing ratio profiles obtained by deconvolution for the mid-day intervals and by trial lineshape fitting for the remaining intervals ,where diminishing S/N ratios provide less reliable deconvolution results.) The high altitude component of ClO is seen to persist throughout the night (about 8 hours duration) with diminished intensity, while the low altitude component appears to drop below the level of detectability by sunset and does not detectably reappear until the time interval 2-4 hours after sunrise, after which it shows a very rapid increase to midday.

In Fig.3 we exhibit a time progression of mixing-ratio profiles consistent

128

C-3

with the synthesized lineshapes (smooth curves) of Fig.2. In this plot, the
vertical lines mark the midpoints of the two-hour time intervals into which the
data was binned. (But note that the mid-day block, as in Fig.2, contains all
data taken at least 6 hours after sunrise and at least six hours before sunset.
This block is ~ 4 hours in length). In Fig. 4, the integrated vertical column
density obtained from the profiles of Fig.3 between 15 and 27 km are shown as a
function of time. The error bars reflect the range of values obtained from
mixing ratio profiles giving equally good fits (within a chosen quality factor)
to the lineshape measurements of Fig.2. Meaningful models of antarctic chlorine
chemistry must meet the constraints imposed by these observations. These results
are in qualitive agreement with recent diurnal modeling reported by Salawitch,
et al.(1988), but do not allow any clear choice between various BrO and ClO
reactions proposed in that work.

References:

Brune,W.H., E.M. Weinstock, and J.G.Anderson, "Midlatitude ClO Below 22 km
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de Zafra,R.L., M.Jaramillo, A.Parrish, P.Solomon, B.Connor, and J.Barrett, "High
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Salawitch,R.J., S.C.Wofsy, and M.B.McElroy, "Chemistry of OClO in the Antarctic
    Stratosphere: Implications for Bromine", Planet. Space Sci., Feb.1988.
Solomon,P.M., B.Connor, R.L.de Zafra, A.Parrish, J.Barrett, and M.Jaramillo,
    "High Concentrations of Chlorine Monoxide at Low Altitudes in the Antarctic
    Spring Stratosphere: Secular Variation", Nature, 328, 411-413, 1987.

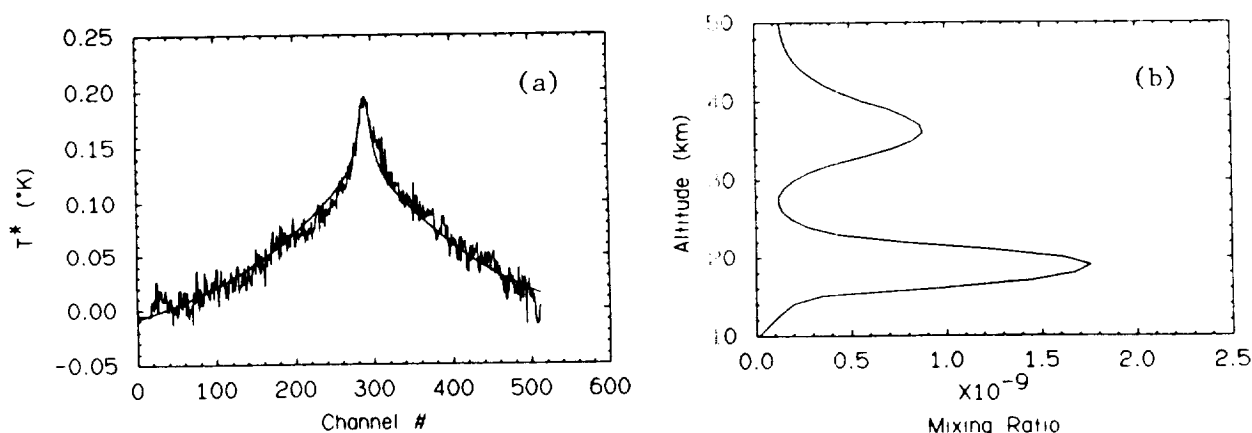Fig.1 a) Midday ClO signal for the period 9/20-24/87. Abscissa is in channel
number, at 1 MHz/channel, ordinate is in degrees equivalent radiative
temperature. Smooth curve is synthesized lineshape given by mixing ratio profile
in (b). b) Mixing ratio profile obtained by deconvolution from data in (a).

j
i
h
g
f
e
d
c
b
a

$T^*$ (°K)

0.2

0    200    400

Channel #

a   b   c   d   e   f   g   h   i   j

50
45
40
35
30
25
20
15
10

ALTITUDE (Kilometers)

a   b   c   d   e   TIME
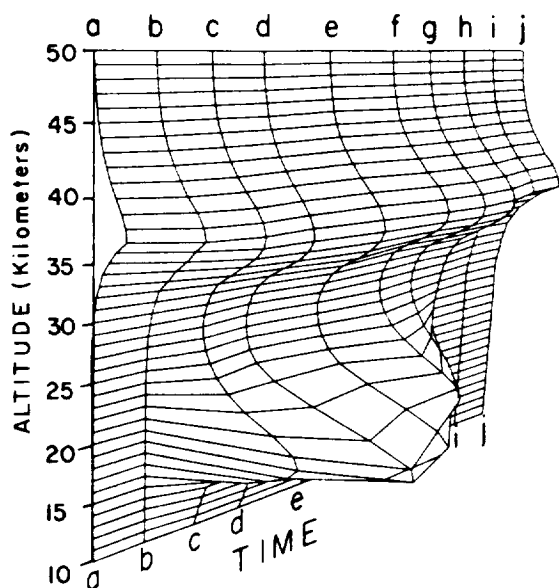
Fig.3 Time evolution of vertical mixing ratio profiles recovered from data. Same profiles generate linefits of Fig.2.

ClO column density (15-27 km)

2.5
2.0
1.5
1.0
0.5
0.0
-0.5

Molecules/cm$^2$x10$^{15}$
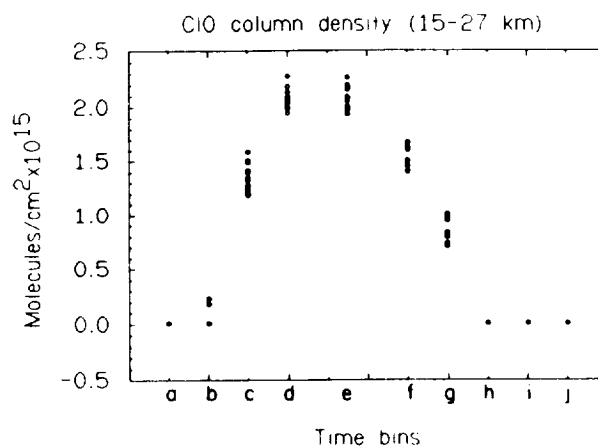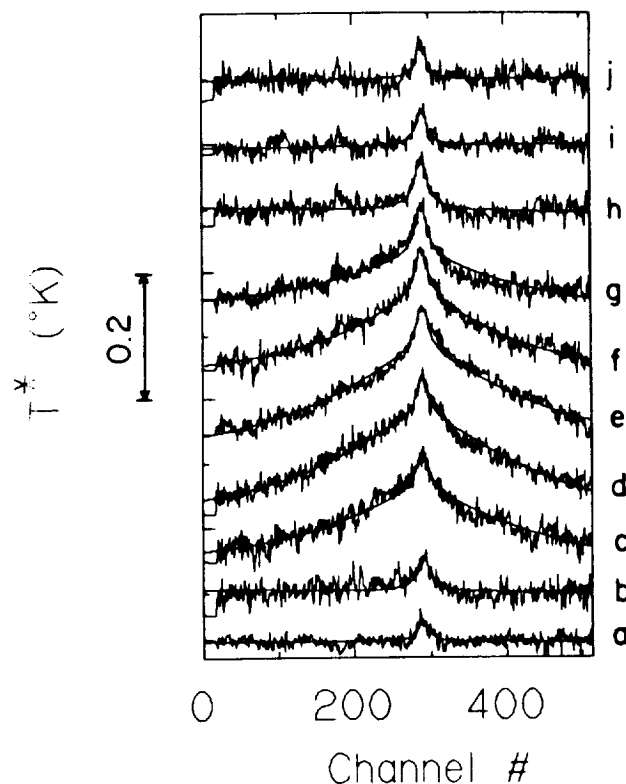
a   b   c   d   e   f   g   h   i   j

Time bins

Fig.4 Integrated column densities of lower altitude components of ClO, obtained from recovered mixing ratio profiles for time-bins of Fig. 2. Range of points represent results from various deconvolutions meeting the same criterion of quality-of-fit to data.

130